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AN AB INITIO COMPUTATIONAL STUDY OF METHANO AND ETHANO BRIDGED DERIVATIVES OF OXYALLYL

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Abstract: Ab initio SCF-CI computations on methano-bridged oxyallyl (OA) **3** and ethano-bridged OA **4** indicate that the OA's are ground state singlet species, with strong C=O bonds and pronounced diradicaloid character in the CI wavefunctions. The computational excited 3B_2 pi-pi* states of **3-4** are ~4-7 kcal/mol higher in energy than the 1A_1 ground state diradicaloids. The bicyclobutanone analog of **3S**, **5**, is predicted to be substantially lower in energy than any of the diradicaloid forms, but the bicyclopentanone analog of **4S**, **6**, is somewhat higher in energy than **4S**. Experimental observation of the triplet manifold of these OA derivatives is likely to be rendered quite difficult by their small singlet-triplet gaps, and the thermodynamic accessibility of the bicyclic analogs. Qualitative molecular orbital considerations suggest that electron-rich olefins might be trapped by a nonconcerted mechanism, in accord with recent experimental results.

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AN AB INITIO COMPUTATIONAL STUDY OF METHANO AND ETHANO BRIDGED DERIVATIVES OF OXYALLYL

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Introduction: Oxyallyl (OA, 1) and related molecules have been discussed as reactive intermediates or transition states in a number of reactions,³⁻⁸ despite an apparent dearth of clear experimental evidence for their direct observation. In such a situation where experiment has been less than clearcut, computational chemical methods can be useful to clarify the problem. Semiempirical and ab initio computational studies have been carried out on OA's, with the most sophisticated published study to date predicting a modest preference for a ground state (GS) π, π^* 3B_2 state⁸ in the parent system 1, despite the possible stabilizing influence on the 1A_1 state of closed-shell zwitterionic resonance structure 2. The computed triplet-singlet (T-S) gap was small enough to leave to question as to whether higher levels of theory might reverse the favoring of a high-spin GS for OA. In addition, consideration of various OA's leads one to query the effects of substitution on the OA state energy ordering, lest by apparently innocuous changes in the OA system one might substantially alter its nature.

[INSERT SCHEME 1]

Two such likely OA derivatives of interest for experimental study are methano-bridged OA 3 and ethano-bridged OA 4 and their ring-closed bicyclic forms 5 and 6. Similar derivatives have been employed in the study of trimethylenemethane⁹⁻¹⁰ (TMM, 7), where the general system 8 has been much studied. Since bridging of 7 to 8 is accompanied by strain incorporation, cyclization is less favorable than for the

unbridged system, making it is easier to study the diradical. Use of methano and ethano bridging in the OA system could in principle lead to a similar favoring of the ring-opened forms 3 and 4. The following computational study is aimed at elucidating the GS multiplicity of 3-4, the approximate stability of the ring-open vs. the bicyclic forms, and the general electronic nature of the bridged OA's. Given recent theoretical¹¹⁻¹² and experimental¹³⁻¹⁴ interest in unusual bond-deficient species that may by various points of view be described as either non-Kekule or nonclassical Kekule molecules, a question of particular interest (also asked by the study of parent OA 1) is whether these OA derivatives are well described as non-Kekule diradicals, or as zwitterions (*e.g.*, 2).

Computational Methods: All computations in this work were done on the University of Massachusetts Department of Chemistry Celerity 1260-D UNIX computer. Geometry optimization for all molecules was carried out using the program GAMESS.¹⁵ For the diradicals, only π - π^* occupancies were studied for open-shell cases, since n - π^* states have typically been found to be substantially higher in energy for cases such as parent OA 1.⁸ Unrestricted Hartree-Fock (UHF) wavefunctions were used for triplet (T) state optimizations, since it has been noted that they generally give a better account of correlation effects in geometry predictions than do restricted open-shell (ROHF) wavefunctions.¹⁶ For the singlet (S) bicyclic molecules 5-6, restricted (RHF) wavefunctions were used for optimization, while for singlet diradicals 3S - 4S two-configuration SCF wavefunctions were used. Computer space considerations prevented our use of multiconfiguration SCF optimization with a reasonable basis set. For the diradicals, C_{2v} symmetry was imposed on the optimizations, with C_s symmetry used for the bicyclic molecules. Standard gaussian split-valence basis sets were used, with modified polarization functions where used. Instead of the usual polarization d-orbital exponent $\alpha = 0.80$ for all atoms in the first

row of the periodic table, *for optimizations only* we used $\alpha_{\text{Carbon}} = 0.75$ and $\alpha_{\text{Oxygen}} = 0.80$.¹⁷ In all cases the rms gradients were reduced to one millihartree/bohr or less.

Once appropriate geometries were found at the various levels of theory, single point configuration interaction (CI) computations were carried out using the MELD series of programs,¹⁸ with standard gaussian basis sets. Excitations up to quadruples (SDTQ-CI) were generated from the ROHF 3B_2 reference for triplets and from a closed-shell 1A_1 reference state that used the TCSCF 1A_1 MO's for singlets. Instead of the canonical virtual orbitals, appropriately transformed K-orbitals¹⁹ were used in the CI to recover correlation energy more efficiently. The active orbital space used for configuration generation for the diradicals in most cases consisted only of pi symmetry MO's. As we shall see, this will lead to an important quantitative limitation to our results, although the qualitative findings should not change. For the bicyclic cases, a variety of mixtures of A' and A'' orbitals was used for SDTQ-CI. The orbital space used for CI computations is described in the tables of results where appropriate.

Results: Figure 1 shows geometric parameters for the 3B_2 and 1A_1 states of 3-4, as well as ring-closed bicyclic forms 5-6, where a modified 6-31G* basis set was used for optimization as described earlier. Complete cartesian coordinate descriptions of these geometries are available in the supplementary material. Table 1 shows a comparison of a selection of geometric parameters for these species as a function of basis set, to allow some evaluation of the differences caused by use of different basis sets in optimization.

[INSERT FIGURE 1, TABLES 1 - 2 ABOUT HERE]

Table 2 shows standard basis set²⁰ 6-31G* SDTQ-CI single point energies in hartrees for the OA diradicals. For 3B_2 diradicals 3T and 4T, excitations were generated from the reference configuration $(1b_2)^2(2b_2)^2(3b_2)^1(1a_2)^1$ to the first nine b_2 virtuals and first six a_2 virtuals, making a total of 10,830 spin-adapted configurations. For the 1A_1 diradicals 3S and 4S, the reference configuration was $(1b_2)^2(2b_2)^2(1a_2)^2$, with

excitations to the first nine b_2 virtuals and the first six a_2 virtuals for a total of 5896 spin-adapted configurations. Other SDTQ-CI active spaces were attempted, but this was the largest permitted by the disk space resources available to us. The potential effects of neglecting sigma-sigma* excitations will be discussed later in this paper.

Table 3 shows the SDTQ-CI energies in hartrees of the bicyclic ketones 5 and 6, using different CI active spaces in each case. The best choice of orbital subspace allowed by our space constraints employed the top three a' MO's, plus either one or two a'' MO's with a selection of virtual orbitals (see table). We feel that the choices of Table 3 that use 21,235 or 40,405 spin-adapted configurations are reasonable estimates of the energies of the bicyclic species relative to their diradical counterparts, since these two computations are energetically comparable for both 5 and 6. Given the number of generated configurations in these cases, it is unlikely that large energy decreases would be realized for the ring-closed forms by increases in the CI active space.

[INSERT TABLE 3]

Discussion: The need for polarization functions in describing OA's is evident by the difference in geometric parameters between optimizations with and without polarization. Much of the stabilization of the 1A_1 state of the OA's comes from a strong C-O bond, which requires polarization to be well described. An earlier study of parent OA by Borden and Morokuma⁸ clearly showed selective stabilization by use of polarization functions of the 1A_1 state with its short C-O bond. In our ensuing discussions we shall only discuss results where optimization and energy SCF-CI computations were both carried out with the 6-31G* split-valence polarized basis set.

Comparison of the 6-31G* geometries for the 3B_2 and 1A_1 states of both ethano and methano bridged OA shows the greater delocalization of the 3B_2 state, as expected by analogy to 3-21G⁸ and more recent²¹ double-zeta with polarization (DZP) MCSCF computations by Borden and Morokuma. The 3B_2 C-O bond lengths for 3T and 4T (123.8 and 126.2 pm respectively) are quite comparable to a recently-computed length of

124.3 pm found by Borden and Morokuma for 3B_2 OA **1** at a DZP-CI level of theory.²¹ The C-C pi-bonds for the 3B_2 state are in relatively good correspondence with the 145.3 pm found by the latter workers.²¹

The 1A_1 diradicals have very short C-O bond lengths, 118.7 and 120.0 pm for **3S** and **4S** respectively. These compare fairly well to the 122.7 pm found by Borden and Morokuma for **1** at the DZP-CI level.²¹ Our C-C bond lengths also compare well to the 146.3 pm found for OA by these workers. The short C-O and reasonably long C-C pi-bonds found by ourselves and the other workers seem to argue against representing OA's with a major component of the zwitterionic resonance structure **2**, which one would expect to have shortened C-C bonds and a fairly long C-O bond. The presence of the short C-O bond implies localization of unpaired electrons on the peripheral carbons of the OA pi-system, and in the case of **1** this has been interpreted as evidence for the diradical (rather than zwitterionic) nature of OA.⁸

Comparison of the four and five-ring cases shows an appreciably shorter C-O bond length for the smaller ring in both 3B_2 and 1A_1 states. If one accepts that the geometric results of Borden and Morokuma²¹ may be directly compared to ours, in the 1A_1 manifold particularly it seems that r_{C-O} decreases as the allyl C-C-C angle decreases. This is logical in terms of hybridization arguments, whereby a decrease in the C-C-C angle will lead to increased s-character in the C-O bond with commensurate C-O shortening.

Energetically, the most notable qualitative result of our results is that both species **3-4** possess singlet ground states (GS's) by modest energetic margins. If one were to accept that OA's are diradicals, Hund's rule predicts a triplet ground state. More sophisticated parity-based qualitative models²²⁻²³ also predict a triplet GS for OA. Recent experimental experience for substituted diradicals seems to indicate that the simple splitting of an orbital near-degeneracy by substitution effects need not make a high-spin GS unachievable. Triplet ground states have been found for *meta*-

benzoquinomethane (9),²⁴ *meta*-naphthoquinomethane^{24,25} (10), and 11,²⁶ all of which possess substantial SOMO splitting even at the simple Huckel level of theory. At times, recent results might seem to tempt one to suspect that any heteroatom-for-methylene substitution in a diradical will leave the GS spin multiplicity qualitatively unchanged, as has been proposed by at least one theoretical model of polyradicals.²³

[INSERT SCHEME 2]

A weakness of this simple assumption may be shown by the following analysis. The larger the energetic splitting between the SOMO's of a diradical system, the larger the energy incurred to keep the electrons spin-parallel in different orbitals, and the more favorable the singlet becomes relative to the triplet. At some point, a critical value must in principle be surpassed where a large HOMO-LUMO gap requires a singlet GS. The question is, what is a large HOMO-LUMO gap and how may one relate this variable to experiment? In the area where the critical value is surpassed, a small difference in the HOMO-LUMO gap changes a molecule qualitatively from triplet to singlet GS. Experimentally, at the present we in almost all cases can find with some confidence only the qualitative GS multiplicity, not the quantitative T-S or S-T energy gap. A decreased T-S gap in a heterosubstituted diradical such as *meta*-benzoquinomethane is expected by qualitative theory, but cannot experimentally be probed at present. It is thus not unlikely that a number of such species that would qualitatively be expected to have reduced T-S gaps have still been observed to have high spin GS's. Sooner or later heterosubstituted species with low spin GS's were bound to be elucidated, based on the argument above. 3,4-Dimethylenefuran 12 and 3,4-dimethylenethiophene 13 are species that computationally¹¹⁻¹² we feel are best defined as diradicals, which experimentally¹³⁻¹⁴ have been found to have singlet ground states. We propose that, like these species, the bridged OA's 3-4 also have crossed the subtle energetic borderland that separates a hetero-substituted diradical

with a Hund's rule high spin GS from a system with sufficient HOMO-LUMO splitting to have a singlet GS.

Qualitative MO considerations show why the bridged OA's are particularly suited to possess HOMO-LUMO splitting sufficient to favor a singlet GS. Figure 2 shows the effect of conceptually activating various orbital effects in OA relative to its hydrocarbon analog, TMM. Oxygen for methylene substitution will qualitatively depress the energy of the symmetric b_1 orbital, leaving the a_2 orbital unaffected to a crude approximation. Decrease of the allyl C-C-C angle due to the constraints of ring formation will reinforce this trend by through-space interactions that will raise the a_2 orbital energy and decrease the b_1 orbital energy. Finally, there will be a through-bond effect of the bridging group in the OA's, which is in opposite directions for the methano vs. ethano bridge. This effect has been predicted by Schoeller to be of potential importance in the bridged TMM cases -- the reader is referred to the literature²⁷ for a more complete description of the direction and nature of qualitative through-bond interactions in the TMM system. Overall, the through-bond effect should be too small to overwhelm the combined effects of substitution and angle contraction in the bridged OA's, and so will be of secondary importance.

[INSERT FIGURE 2]

The previous analysis may be confirmed in a crude qualitative manner. We carried out RHF singlet computations upon the singlet GVB geometries of 3S and 4S as a measure of HOMO-LUMO splitting in the four vs. five-member ring systems. We found at the 6-31G* level that the pi HOMO-LUMO gap for 3S was $-(-0.302 - -0.015) = 0.287$ hartrees or 7.8 eV. For 4S the analogous gap is $-(-0.251 - -0.120) = 0.131$ hartrees or 3.6 eV. Since the actual CI computations are based upon TCSCF MO's, it would be wrong to overinterpret these RHF numbers, but in terms of the crude HOMO-LUMO gap analysis the trend of increased gap with decreased C-C-C angle is obvious.

Borden and Morokuma's results to date²¹ indicate that parent OA 1 retains a small preference (~1 kcal/mol) for a 3B_2 GS, in agreement with the qualitative connectivity models.²²⁻²³ Given the influence of angle contraction in the bridged OA systems, our computed S-T gaps of ~4-6 kcal/mol seem quite in line with the qualitative MO arguments above. Thus, it seems less surprising that, despite substantial efforts, there is to our knowledge no direct experimental evidence for observation of a triplet OA species. Based on our SCF + pi-SDTQ-CI results, OA simply appears to be a system where HOMO-LUMO splitting reduces the T-S gap until small effects such as bridging and C-C-C angle may reverse the "expected" triplet GS preference. This effect is reinforced in the bridged OA's by the previously mentioned (*vide supra*) hybridization effects which shorten and strengthen the C-O bond, favoring the 1A_1 state more than in unbridged 1.

Sigma-sigma* excitations were not used in our CI computations due to the space requirements of such computations at the SDTQ-CI level. For these systems the cumulative effect of such excitations would be large. In computational studies of hydrocarbon pi-diradicals, sigma-pi orbital energy separability could be assumed without major errors in relative state energies.²⁸ However, a study of formyloxy 14 by Borden, Davidson, and Feller²⁹ clearly showed that sigma excitations can be important for even a qualitative description of state ordering in an open shell system where a heteroatom may bear unpaired spin. Such considerations could confound our study with only pi-excitations, due to the energetically high lying lone pair orbital of the OA system (Figure 2).

[INSERT SCHEME 3]

Results for the oxyallyl parent system suggest that, while one may question the quantitative S-T gaps in our study, still the qualitative GS spin multiplicity -- the only property presently verifiable by experiment -- will be as we predict. SDTQ-CI 6-31G* computations by us on 1 with pi-only excitations and sigma+pi excitations clearly show

a selective stabilization of the 1A_1 state relative to the 3B_2 state for the sigma+pi schemes. Recent higher level computations on **1** confirm this trend.²¹ Since our pi-only CI results already predict a 1A_1 GS for both **3** and **4**, we feel that inclusion of sigma excitations with their commensurate demands in CPU time and disk space are not required to answer the experimental prediction of the GS spin multiplicity of the bridged OA's.

One may argue that the bridged OA's at least should not be classified as diradical, non-Kekule species, but as some sort of zwitterionic, Kekule species such as the resonance structure **2** shown earlier. Aside from the the evidence of our optimized geometries, which seems not to support this argument, we note that the CI wavefunctions describing the 1A_1 ring-opened structures **3S** and **4S** indicate intermediate diradical character. Borden has used the square of the ratio of the two largest coefficients C_1 and C_2 in the CI wavefunction of a singlet species as a relative measure of diradical nature.¹² Where C_1 and C_2 are comparable ($[C_1/C_2]^2 \sim 1.00$), a two-configuration wavefunction is required for a good electronic description of the molecule, which is a hallmark of a diradical. For a Kekule species that is well described by a single electronic configuration, $C_1 \gg C_2$, and $[C_1/C_2]^2 \gg 1.00$. For the 1A_1 bridged OA's **3S** and **4S**, $[C_1/C_2]^2$ is 4.16 and 4.05 respectively. This is greater than the 1.00-2.50 range that one might expect for a nearly "pure" diradical, but still indicates substantial diradical character. Borden found that $[C_1/C_2]^2 = 1.73$ for the putative diradical **12**, but a value of 5.06 for carbonyl ylid **15**.¹² By this comparison our OA's are more diradicaloid than carbonyl ylid, but less so than 3,4-dimethylenefuran and related compounds.

Alternatively, one can consider the occupation numbers of the CI natural orbitals (NO's), which can reflect the diradical nature of the two SOMO's³⁰ without the extreme sensitivity to small changes in C_1 and C_2 that affect the ratio $[C_1/C_2]^2$. We find the 1A_1 ring-open OA's **3S** and **4S** to have 6-31⁺ SDTQ-CI $3b_1/1a_2$ NO occupancies

of 1.608/0.390 and 1.549/0.401. These results agree with the ratio-squared results in showing an intermediate range of diradical behavior for the bridged OA's. A "pure" diradical would have SOMO₁/SOMO₂ NO occupation numbers of 1.00/1.00, while a Kekule molecule would have a SOMO₁ occupancy of ~2.00 and a SOMO₂ occupancy of ~0.00. We find that parent OA at a similar level of theory has NO occupation numbers in the ¹A₁ state of 1.37/0.64, showing substantially more diradical nature than the bridged species. By our results, OA's might best be described as diradicaloid, but less so than a classical diradical such as TMM.

In experiments generating diradicals, it has often been of importance to evaluate the role of potential ring-closed products that could deplete the ring-open form population. For instance, the role of bicylopentane 8 in the chemistry of the ethano-bridged TMM system 7 is experimentally quite important.⁹ Our results suggest that the ring-closed systems 5 and 6 are thermodynamically quite competitive with the ring-open states. For the five-member ring case, the bicyclopentanone 6 lies between (+3.0 kcal/mol) the GS diradicaloid ¹A₁ and ³B₂ states. For the four-member ring case, the bicyclobutanone 5 lies a surprising 34 kcal/mol below the ¹A₁ diradicaloid.³¹

[INSERT FIGURE 3]

A study analogous to ours for OA was carried out by Dixon and coworkers for ethano³² and methano-bridged³³ TMM. In this study, the ring-closed 8 was found to lie 10 kcal/mol higher than the ³B₂ diradical TMM 7, with the ¹A₁ state 19 kcal/mol above the ³B₂ (Figure 3). By comparison, methylenebicyclobutane 17 was found to be essentially degenerate with the analogous ³B₂ TMM 16, and most likely lies even lower in energy due to the basis set level used in this computation: the ¹A₁ state of 16 lies approximately unchanged relative to the ³B₂ at +22.0 kcal/mol.

The stabilization of the ring-closed form relative to the diradicals by methano *vs.* ethano bridging for the TMM's and OA's is analogous, for reasons that are probably based upon the ring strain in 3 relative to 4. In the methano bridged system, both the

OA and the ring-closed form retain a substantial amount of small-ring strain which will tend to cancel in considering the gap between the open and closed forms. In this case, the extremely short C-O bond and extra C-C bond in 5 will cause it to be favored thermodynamically over the open form 3. In the ethano bridged system, presence of the short C-O bond and extra C-C bond in 6 will be offset in the open form 4 by a lack of major ring strain in the five-member ring. As a result, one might expect the closed and open five-member ring forms to be energetically more comparable by this analysis than is the case for the four-member ring case, as is predicted by our computations. The high degree of strain in the OA 3 and the relative stability of the closed form 5 would seem to render the four-member ring OA system to be a less attractive experimental target than the five-member ring. In a similar attempt to study the methano-bridged TMM system 16,¹⁰ no evidence for a TMM was obtained, but only unrelated products apparently derived from a thermally allowed bicyclobutane to butadiene rearrangement of 17.

Zwitterionic OA systems have been widely invoked as a key reactive intermediate in the photoisomerization of cross conjugated dienones (equation 1).³⁴

[INSERT SCHEME 5]

The evidence supporting the intermediacy of a zwitterionic species rests largely on the results of trapping studies with nucleophiles such as alcohols and halides³⁵ The photoreaction can give a variety of deep seated rearrangements and fragmentation products that are highly dependent on both the structure of the dienone and the reaction medium. An OA zwitterion has been suggested as an observable intermediate that is stable at reduced temperature in some related photochemical solution phase work.³⁶ Observation of the dienone photorearrangement in the gas phase has in some cases been interpreted as meaning that the isomerization may proceed through a diradical and not a zwitterionic intermediate.³⁷ The zwitterionic interpretation of the photoreaction may also be consistent with our description of the ground state of 4 as

being diradicaloid, rather than a true diradical. It is possible that a polar reaction medium may cause an altering of reactivity such that trapping chemistry is observed that is consistent with that usually interpreted as being from a zwitterionic molecule.

Recently one of us has conducted an olefin trapping study supporting the intermediacy of a bridged OA system (equation 2 below).³⁸ Photochemical irradiation of 18 at reduced temperature leads to a storable new reactive molecule, believed to be the isomer 19. The likely presence of OA 20 is deduced by the lack of olefin trapping products attributable to trapping by 19, but only of products logically derivable from 20, possibly by a zwitterionic or diradical mechanism. To our knowledge, this is the first example of the capture of a putative OA system by a simple mono-olefin, although conjugated dienes have been observed to give [3+4] adducts with OA intermediates.³⁹

[INSERT SCHEME 6]

The experimental results of the olefin and diene trapping studies is reasonable in terms of simple molecular orbital (MO) models of OA. As shown earlier in Figure 2, the OA HOMO will be of b_2 symmetry, the LUMO of a_2 symmetry. Since the HOMO is substantially lowered relative to the HOMO of TMM, one might expect OA's to act more as electron acceptors than TMM's, as observed experimentally (equation 2, above). Equation 3 shows the interaction of the HOMO of an electron rich olefin with the LUMO of an OA. A concerted cycloaddition cannot occur with these MO's, hence a stepwise zwitterionic or diradical path is likely, as postulated in experimental studies. The finding of fused *and* bridged adduct-type products in the reaction of equation 2 is consistent with such a stepwise mechanism. As a result, one might expect stereochemical scrambling in trapping studies where such effects might be monitored. Experimental studies are underway by one of us to test the stereochemical outcome of olefin trapping by OA's, and will be reported in due course.

[INSERT SCHEME 7]

Summary and Conclusions: This computational study of model bridged oxyallyl derivatives highlights several characteristics of these species which are worthy of experimental verification as part of the present interest in elucidating factors determining ground state multiplicity and electronic nature in diradicals and related bond deficient species.

(1) Both methano and ethano bridged OA's favor a 1A_1 ground state with a strong C-O bond. Structurally, they do not appear to be well-described by a set of zwitterionic resonance structures such as 2, but rather by diradicaloid structure 1 with unpaired electron density on the periphery carbons of the pi-system. Efforts to observe the low-lying 3B_2 state are likely to be impeded by energetically favorable intersystem crossing to the singlet manifold, aided by spin-orbit coupling due to the presence of the oxygen atom.

(2) The bridged OA's, although they possess a fair degree of diradical nature in their CI wavefunctions, at our level of theory seem to be better described as diradicaloid singlet molecules, rather than true diradicals. This conclusion is based on a comparison of our ab initio CI wavefunctions to those computed by others for heteroatom-containing bond-deficient species.

(3) The bicyclic species 5-6 are of potential experimental importance for methano and ethano bridged systems. The stability of bicyclobutanone 5 is so great relative to the ring-open species 3S and 3T is such that efforts to observe the latter are likely to be extremely difficult unless a high barrier to ring closure of 3S to 5 exists. Given the allowed nature of this cyclization, such a barrier seems fairly unlikely. The relative stability of bicyclo-pentanone 6 is similar to that of the ring-open forms of OA 4, hence the potential role of 6 in the chemistry of the five-member ring OA's is not clear.

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Supplementary Material available for this paper consists of 6-31G* optimized structures (Cartesian coordinates).

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Table 1

Comparison of Selected Geometric Parameters as a Function of Basis Set for Bridged Oxyallyl Systems 3-4.

| Molecule | Parameter | 3-21G ^a | 3-21G(*) ^{a,b} | 6-31G ^a | 6-31G* ^a |
|----------|------------------------------------------------|--------------------|-------------------------|--------------------|---------------------|
| 3 UHF | C ₁ -O | 128.2 | 123.4 | 128.3 | 129.8 |
| | C ₁ -C ₂ | 144.7 | 144.8 | 143.9 | 144.0 |
| | C ₂ -C ₃ | 154.7 | 152.6 | 153.3 | 151.9 |
| | C ₁ -C ₂ -C ₃ | 92.8 | 92.0 | 93.0 | 92.2 |
| | C ₂ -C ₃ -C ₄ | 85.3 | 86.0 | 85.8 | 86.1 |
| | C ₄ -C ₁ -C ₂ | 90.9 | 91.0 | 90.6 | 90.9 |
| | | | | | |
| 3 TCSCF | C ₁ -O | 120.6 | 119.5 | 121.8 | 118.7 |
| | C ₁ -C ₂ | 148.6 | 143.7 | 146.6 | 146.0 |
| | C ₂ -C ₃ | 154.6 | 151.4 | 153.4 | 152.2 |
| | C ₁ -C ₂ -C ₃ | 87.9 | 85.5 | 88.4 | 87.8 |
| | C ₂ -C ₃ -C ₄ | 83.7 | 80.2 | 83.5 | 88.4 |
| | C ₄ -C ₁ -C ₂ | 94.2 | 97.2 | 94.0 | 94.4 |
| | | | | | |
| 4 UHF | C ₁ -O | 130.9 | 126.2 | 130.6 | 126.5 |
| | C ₁ -C ₂ | 141.8 | 142.3 | 141.9 | 142.1 |
| | C ₂ -C ₃ | 151.4 | 150.1 | 150.8 | 150.0 |
| | C ₃ -C ₄ | 157.5 | 156.0 | 156.5 | 155.7 |
| | C ₃ -C ₄ -C ₂ | 110.4 | 109.5 | 110.5 | 109.7 |
| | C ₅ -C ₁ -C ₂ | 110.4 | 110.5 | 110.0 | 110.3 |
| | C ₁ -C ₂ -C ₃ | 104.4 | 104.8 | 104.7 | 104.8 |
| | C ₂ -C ₃ -C ₄ | | | | |
| 4 TCSCF | C ₁ -O | 122.1 | 119.1 | 123.5 | 120.0 |
| | C ₁ -C ₂ | 146.1 | 145.9 | 144.9 | 144.8 |
| | C ₂ -C ₃ | 149.7 | 148.6 | 149.4 | 148.6 |
| | C ₃ -C ₄ | 156.1 | 154.6 | 155.0 | 154.2 |
| | C ₃ -C ₄ -C ₂ | 103.9 | 103.5 | 104.5 | 103.8 |
| | C ₅ -C ₁ -C ₂ | 94.2 | 97.2 | 94.0 | 94.4 |
| | C ₁ -C ₂ -C ₃ | 83.7 | 80.2 | 93.5 | 88.4 |
| | C ₂ -C ₃ -C ₄ | | | | |

^aBond lengths in picometers, bond angles in degrees. Optimization performed as described in the

paper. ^bStandard 3-21G basis set augmented by polarization functions on carbon and oxygen as in Harihan,

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Table 2

6-31G* SDTQ-CI Ab Initio Energies of Oxyallyl Species 3-4.

| Structure ^a | Energy ^b | Spin Adapted Configurations (Mult) ^c | S-T Gap ^e |
|------------------------|---------------------|----------------------------------------------------|----------------------|
| 3 UHF | -228.58415 | 10,830 (T) ^d | 4.0 |
| UHF | -228.58421 | 5,896 (S) | |
| GVB | -228.58185 | 10,830 (T) | |
| GVB | -228.59061 | 5,896 (S) ^d | 0.0 |
| 4 UHF | -267.64878 | 10,830 (T) | |
| UHF | -267.66415 | 5,896 (S) | |
| GVB | -267.65924 | 10,830 (T) ^d | 6.9 |
| GVB | -267.67018 | 5,896 (S) ^d | 0.0 |

^aSee Figure 1 for structural parameters. ^bEnergy in hartrees (1 hartree = 27.21 eV = 627 kcal/mol) from 6-31G* SDTQ-CI computation. ^cSpin adapted configurations generated by MELD and used in SDTQ-CI computation for the indicated multiplicity at the indicated fixed geometry. ^dLowest energy computed for the indicated multiplicity. ^eEnergy in kcal/mol relative to lowest energy of lowest state.

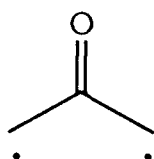
Table 3

Selected 6-31G*^{*} SDTQ-CI Energies for Bicyclic Compounds 5 and 6.

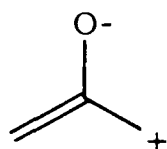
| Structure ^a | Energy ^b | Spin Adapted Configurations (MO's) ^c |
|------------------------|---------------------|-------------------------------------------------------------|
| 5 | -228.63359 | 28,804 ([11a' - 13a'] => 7xa') (5a'' => 4xa'') |
| | -228.63859 | 40,405 ([11a' - 13a'] => 7xa') (5a'' => 5xa'') |
| | -228.64546 | 21,235 ([11a' - 13a'] => 5xa') ([4a'' - 5a''] => 3xa'') |
| 6 | -267.66470 | 21,235 ([12a' - 14a'] => 5xa') (7a'' - 8a'' => 3xa'') |
| | -267.66537 | 40,405 ([12a' - 14a'] => 7xa') ([8a''] => 5xa'') |

^aSee Figure 1 for geometries. ^bEnergy in hartrees (1 hartree = 27.21 eV = 627 kcal/mol). ^cNumber of spin-adapted configurations generated by MELD, using the CI active space noted. [X a'' - Y a''] => Zxa'' means the electrons in orbitals of a'' symmetry numbered X - Y are excited up the the quadruples level into the lowest lying Z a'' virtual orbitals (as well as other virtuals in the overall active space).

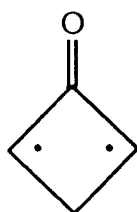
Scheme 1



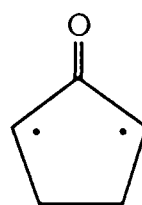
1



2



3



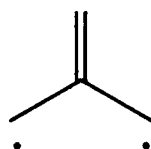
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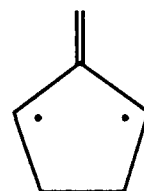
5



6

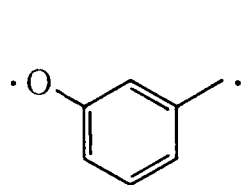


7

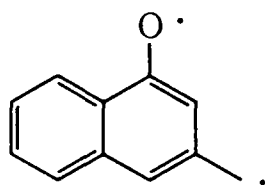


8

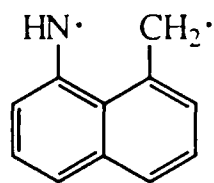
Scheme 2



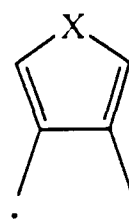
9



10



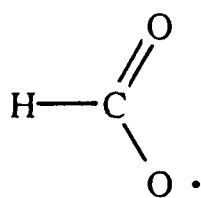
11



12 X = O

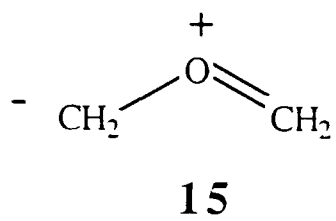
13 X = S

Scheme 3

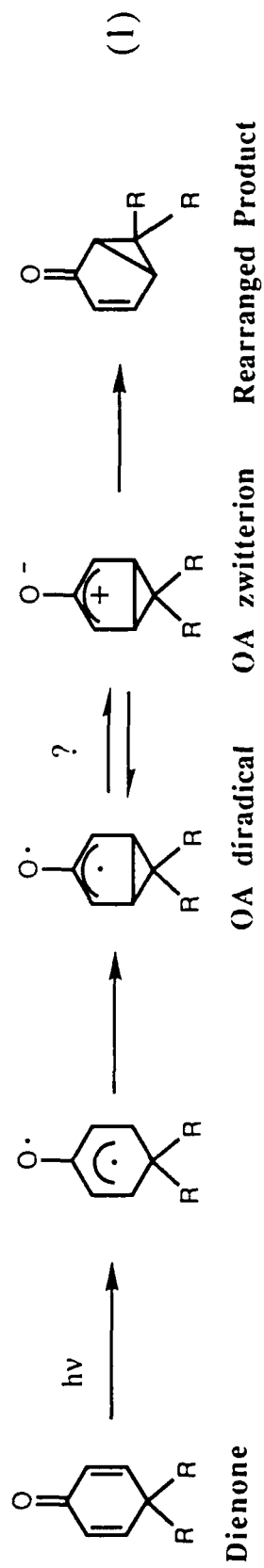


14

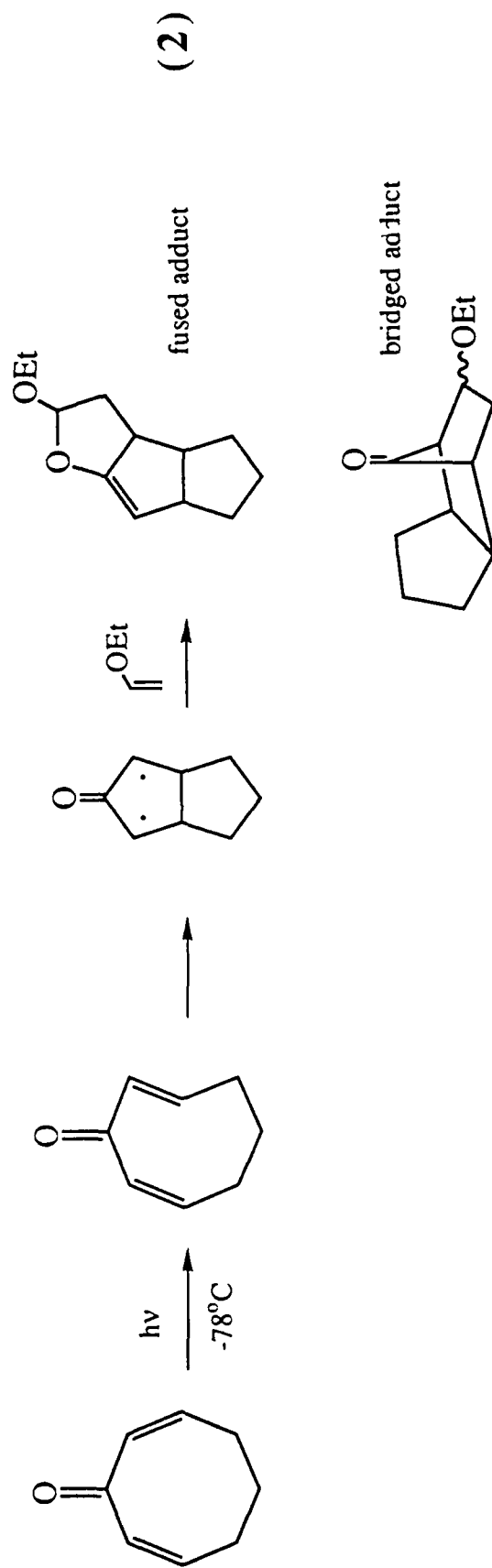
Scheme 4



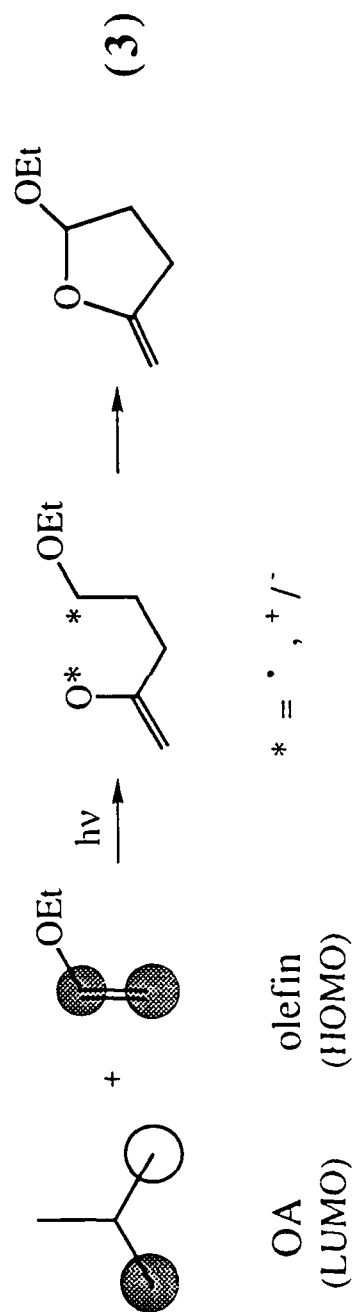
Scheme 5



Scheme 6



Scheme 7



CAPTIONS AND LEGENDS FOR FIGURES

Figure 1.

Caption: 6-31G* Ab Initio Predicted Geometries for Bridged Oxyallyls and Kekule Isomers.

Legend: Bond Lengths are in picometers, bond angles in degrees (underlined). 3B_2 geometries obtained using UHF wavefunctions, 1A_1 diradical geometries using TCSCF wavefunctions, bicyclic geometries using RHF wavefunctions. Full geometric details are listed in supplementary material.

Figure 2.

Caption: Perturbation Effects Upon Frontier Molecular Orbitals in Bridged Oxyallyls Relative to Trimethylenemethane.

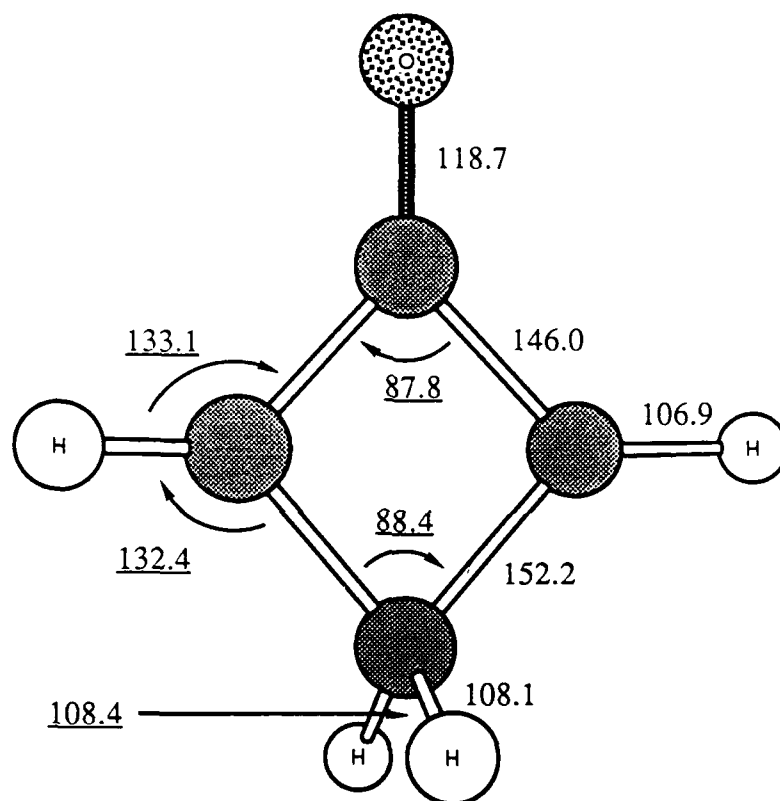
Legend: All effects shown are qualitative and not to scale. The smaller effects of through bond coupling by ethano vs. methano bridging of oxyallyl are not included. Cf. ref. 27 for a discussion of this effect.

Figure 3.

Caption: Comparison of Relative Energies for Methano vs. Ethano Bridged Trimethylenemethane, Oxyallyl, and Kekule Isomers.

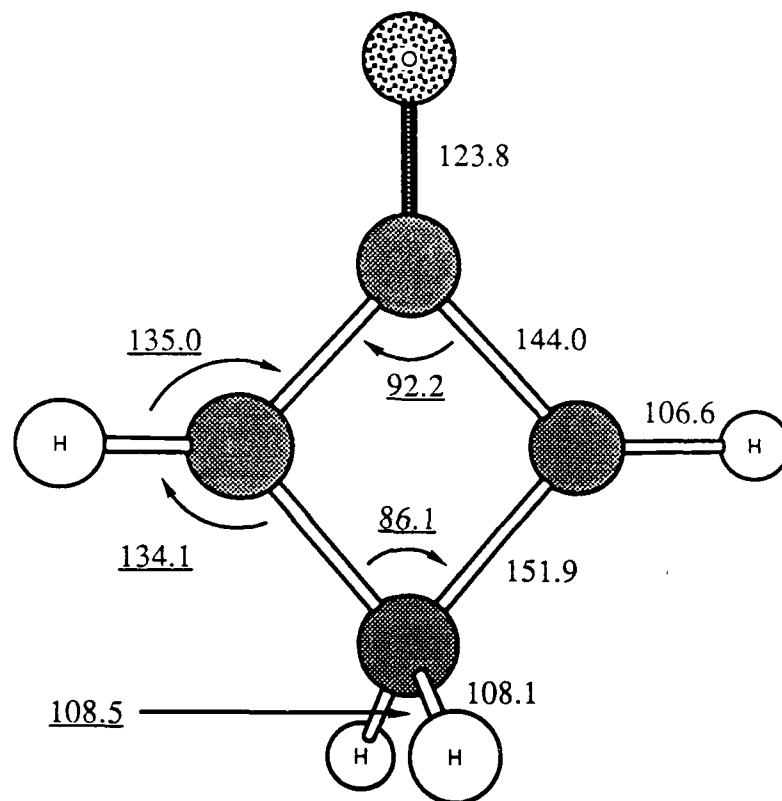
Legend: The reference zero of energy in each comparative scheme is chosen arbitrarily to allow relative comparisons between different species -- no comparison of absolute energies between different species is implied in the scheme. Energies are relative to the zero energy in each species, kcal/mol. bond = Kekule isomer. Energies for the trimethylenemethanes are from refs 32-33.

Figure 1



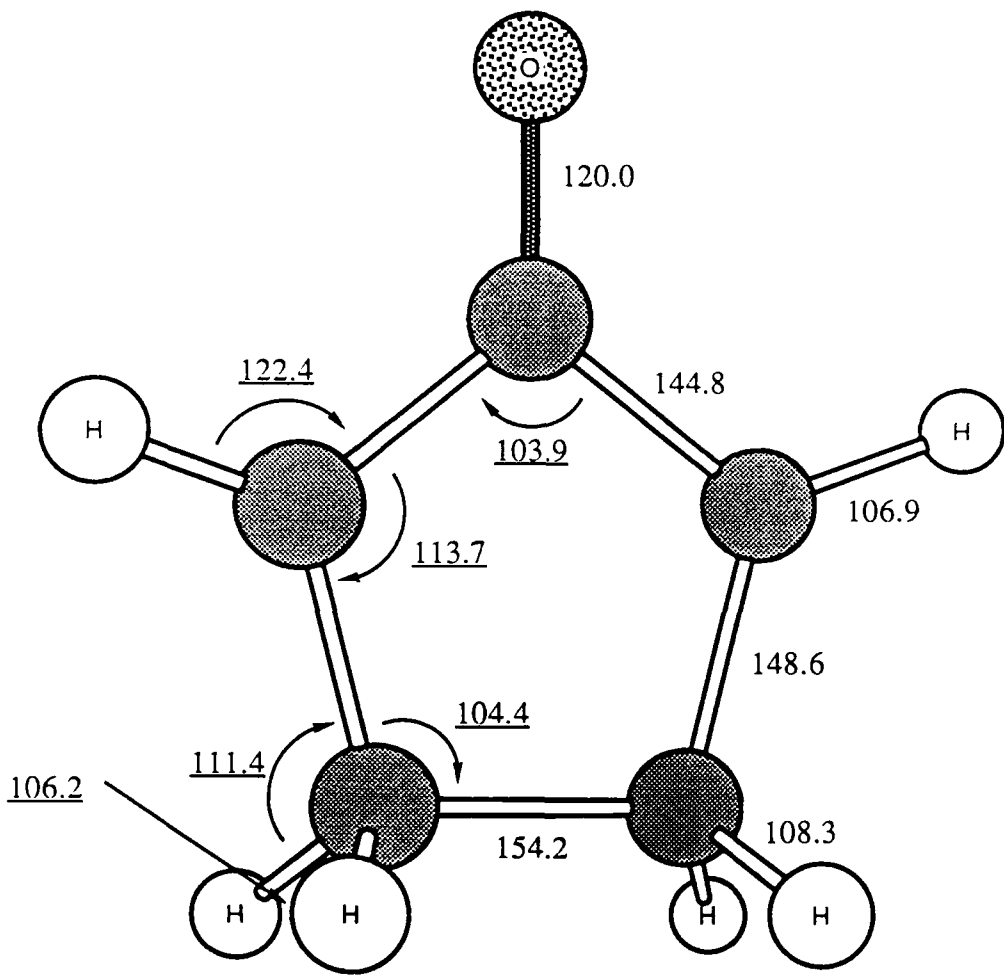
3S (1A_1 TSCF)

Figure 1 (continued)



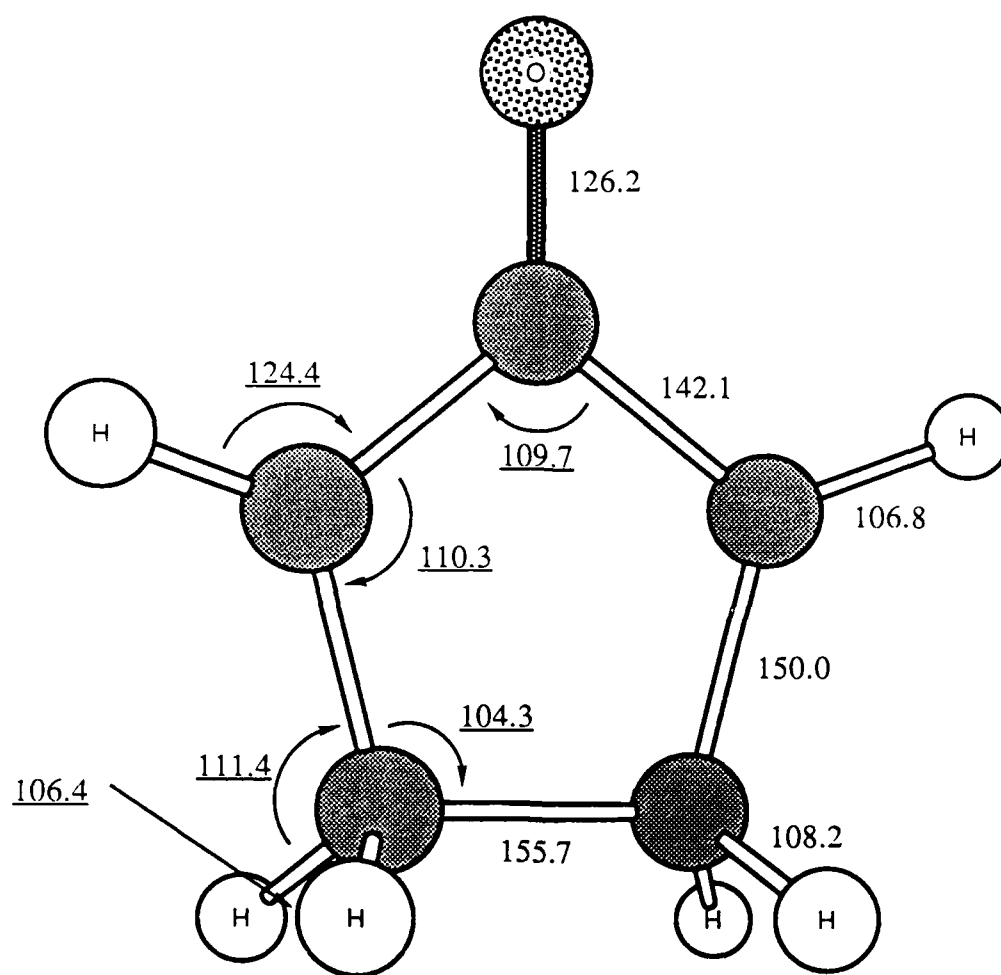
3T (3B_2 UHF)

Figure 1 (continued)



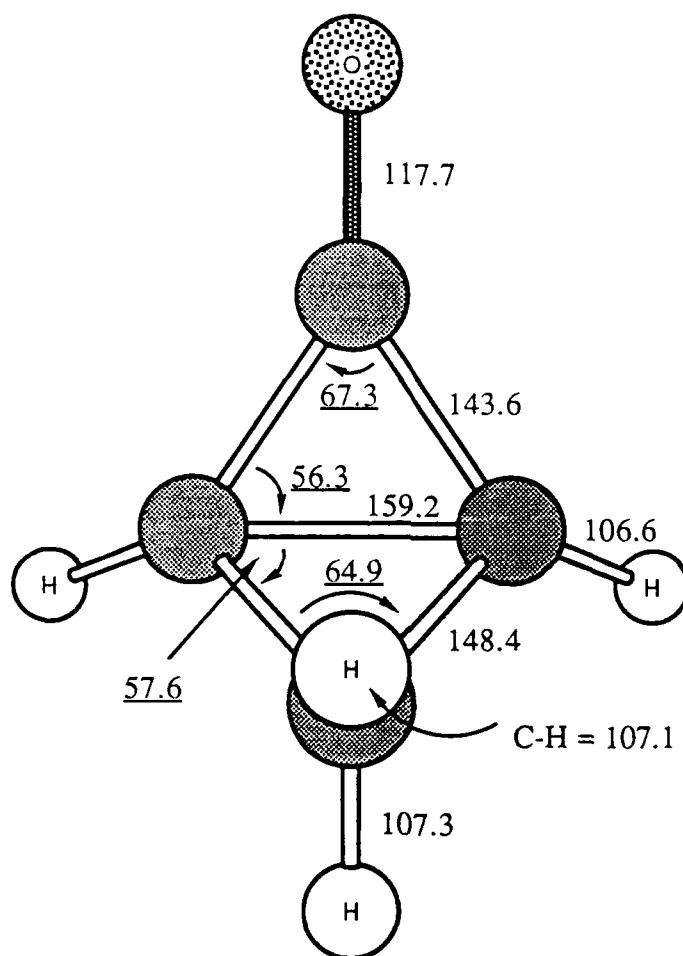
4S (1A_1 TCSCF)

Figure 1 (continued)



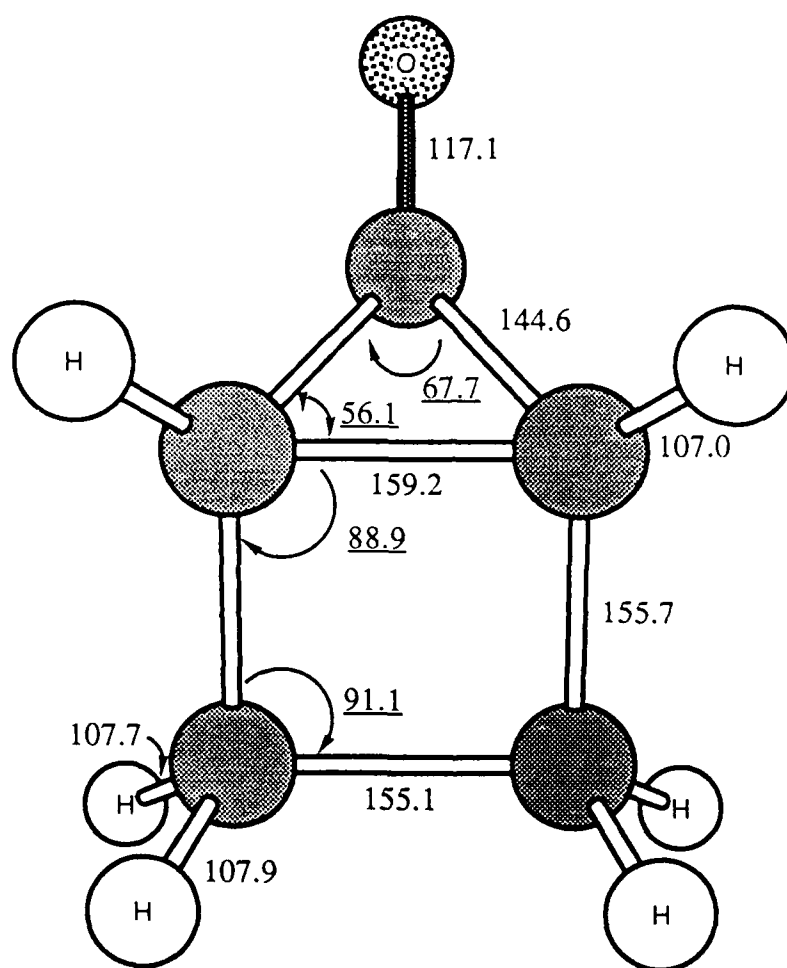
4T (3B_2 UHF)

Figure 1 (continued)



5 ($^1A'$ RHF)

Figure 1 (continued)



6 (¹A' RHF)

Figure 2

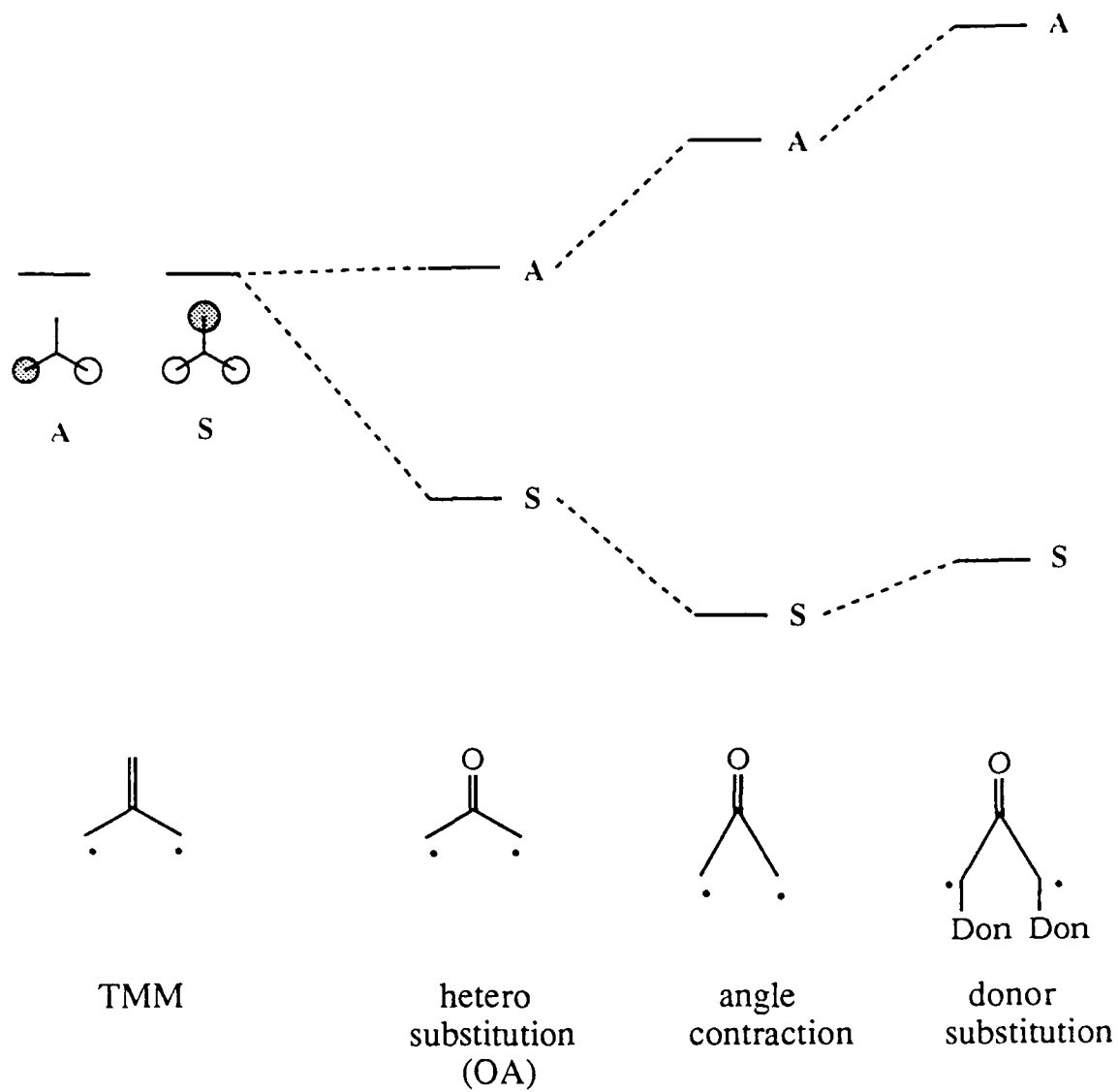


Figure 3

